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13. SUPPLEMENTARY NOTES**14. ABSTRACT**

This research program explores time-resolved dynamics of molecular systems using femtosecond core level photoelectron spectroscopy. Ultrafast soft x-ray laser pump/probe studies reveal time-dependent binding energies and atomic core level shifts in the molecules during chemical rearrangements by detecting the changes in photoelectron spectra as a function of internuclear separation in dissociative states in real time. A new apparatus introduces high order harmonics of a laser in the soft x-ray region of the spectrum. Harmonic pulses with photon energies up to 100 eV and femtosecond time resolution have been produced with excellent efficiency and pulse-to-pulse stability. Valence and core photoelectron spectra have been obtained on many neutral atoms and molecules with this apparatus.

15. SUBJECT TERMS

Femtosecond x-ray laser, x-ray photoelectron spectroscopy, Harmonic generation, photoionization

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Final Report
"Ultrafast Soft X-ray Laser Probing of Core Level Molecular Dynamics"

Stephen R. Leone, Veronica M. Bierbaum - Principal Investigators

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Executive Summary

This is a program of experimental measurements in ultrafast laser soft x-ray studies of the reactions and dynamics of molecular precursors to metal/oxidizer fuel components of rockets and related species. A new apparatus produces high order harmonics of a laser in the x-ray region of the spectrum with ultrafast pulse durations and is used to measure valence orbitals and atomic core level shifts by time-resolved photoelectron spectroscopy (PES) and x-ray photoelectron spectroscopy (XPS) during reactions and dissociation. The apparatus consists of a 2.5 mJ pulse, 1000 Hz repetition rate Ti:sapphire laser system, a 1000 Hz pulsed jet of rare gas species for harmonic generation, harmonic separation by a dual grazing incidence gratings for temporal recompression, a vacuum chamber for sample introduction, and a magnetic bottle time-of-flight electron spectrometer for kinetic energy analysis of the resulting photoelectrons. High order harmonics of the Ti:sapphire laser up to the 65th (≈ 100 eV) are produced with excellent efficiency and characterized in detail with respect to laser power density, chirp, and efficiency. Ultraviolet and soft x-ray (core level) photoelectron spectra are obtained on a large variety of neutral atoms and molecules in this table top laboratory setup. The first ultrafast pump-probe experiments were performed on a dissociative state of Br_2 molecules. The ability to time-overlap a pump pulse and an x-ray probe pulse was developed, and cross correlations as short as 180 fs are achieved. Measurements were performed with the 13th, 15th, 17th, 19th, and 21st harmonics as the probe. Multiple features are observed in the dissociating bromine system. These include: above threshold ionization processes, the formation of the final atomic state transitions on 40 fs timescales, and a short-lived wave packet on the dissociative state. Estimates of the relative cross sections for above threshold ionization compared to the ionization of the direct wave packet on the dissociative state are obtained. Preliminary measurements are obtained for the photoelectron spectrum of the moderately long-lived B electronic state of bromine molecule.

A. Apparatus for Ultrafast Soft X-Rays

Recent developments in ultrafast laser generation of high-order harmonics in rare gases now offer excellent opportunities to the experimentalist for tabletop soft x-ray investigations. Until recently, these laser sources were primarily the domain of laser groups working on the harmonic generation process itself. These tools can now be used to address a large number of intriguing chemical and materials problems of wide interest. High harmonic sources can produce up to 600 eV photon energies, with bandwidths comparable to synchrotron sources and photon fluxes of as much as 10^{10} per second, depending on wavelength.

The apparatus constructed with AFOSR support for ultrafast soft x-ray research is illustrated in Fig. 1. It consists of a 1000 Hz Ti:sapphire laser that produces 2.5 mJ per pulse at 800 nm with pulses of 70 fs duration, a piezoelectric pulsed valve, also operating at 1000 Hz, to form the jet of high density rare gas that is used as the nonlinear harmonic medium, a vacuum chamber to introduce gaseous samples, and a time-of-flight magnetic bottle electron spectrometer. In addition, the apparatus has frequency doubling and tripling of the Ti:sapphire fundamental pulse in nonlinear crystals to generate a separate photolysis pump pulse, an optical delay line, two grazing incidence gratings for wavelength separation to select individual harmonics and to recompress the temporal characteristics of the x-ray pulses, a quadrupole mass spectrometer for ion mass detection, and necessary pulse autocorrelation measurement tools.

The philosophy in constructing the apparatus was to make a source of femtosecond soft x-rays that would operate at high repetition rate (1000 Hz), not necessarily state-of-the-art in terms of short pulse duration, photon energy (harmonic number), or pulse energy, but reliable, so that the system operates indefinitely and on a daily basis. This necessitates a very stable Ti:sapphire laser system consisting of a seed laser, regenerative amplifier, and two-pass amplifier. In order to maintain reasonable spectral bandwidths of the harmonics, a longer pulse of 70 fs was chosen, and bandwidths of 0.1-0.4 eV are routinely achieved²² on individual harmonics. Since the path of the x-rays is not easily altered, only grazing incidence gratings are used to select one harmonic and the delay line manipulations are carried out in the pump beam path (see Fig. 1). We also plan to take advantage of newly-discovered aspects of x-ray formation, such as phase shaping of the input pulse with learning algorithms to enhance harmonics.

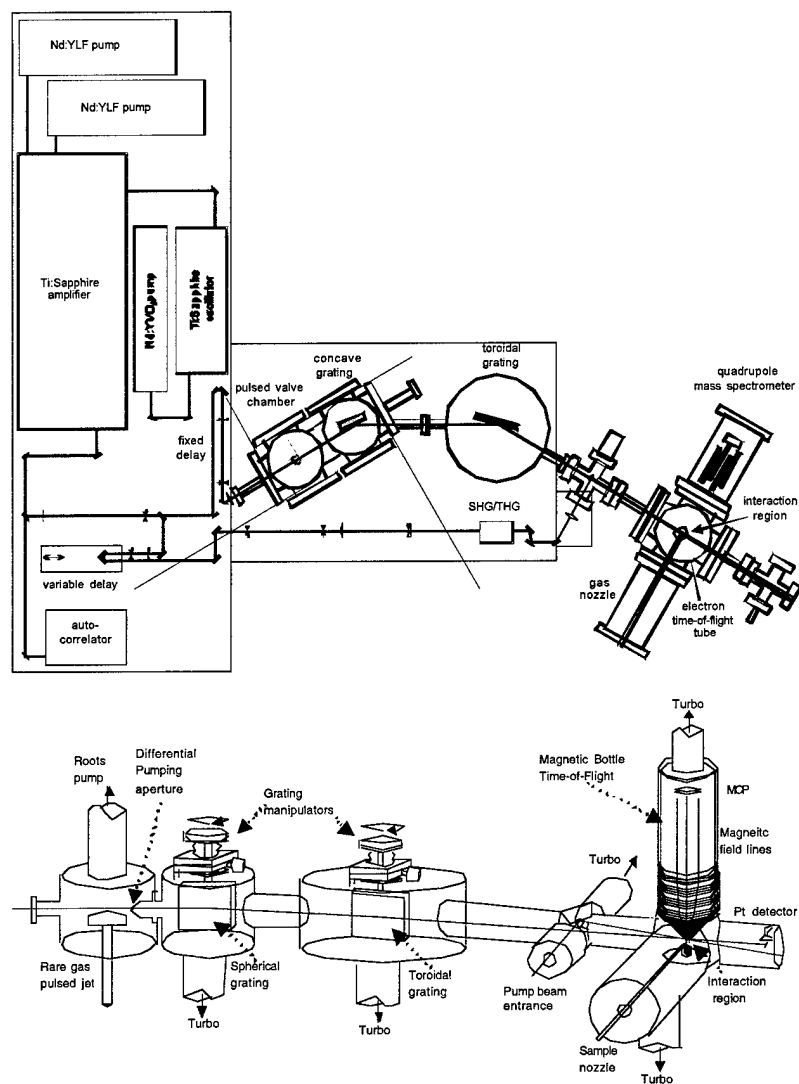


Figure 1. Apparatus for generating high order harmonics for photoelectron spectroscopy and pump/probe time-resolved studies with x-ray harmonics.

The production of high order harmonics in rare gases is a different mechanism than the usual sum and difference frequency or four wave mixing in nonlinear optics. The laser is focused to 10^{14} - 10^{15} W cm $^{-2}$ in a high density of a rare gas ($\approx 10^{18}$ cm $^{-3}$) in a pulsed jet. The process qualitatively involves driving an electron away from the ionic core of the rare gas and then, on the opposite cycle of the light, driving the electron back into the core, whereupon the harmonic light is generated. The light is produced with similar efficiency over a large number of odd harmonics up to some cutoff energy. The fact that only odd harmonics are produced results from symmetry considerations in an isotropic medium. With our apparatus, harmonics of 800 nm are produced (Fig. 2) up to the 65th (≈ 100 eV) and can be used for static photoelectron spectroscopy with excellent signal-to-noise (100:1 in minutes). Many details about generating and optimizing the high harmonic process were investigated, including the effect of pulse chirp on the harmonic spectra (chirp is the process where the frequency of the ultrafast pulse sweeps from high to low or low to high over the duration of the pulse). Moreover, the output of the system is stable enough to take two spectra, one with a pump laser on and one with a pump laser off, and reliably subtract them to obtain the small differences induced by the pump laser.

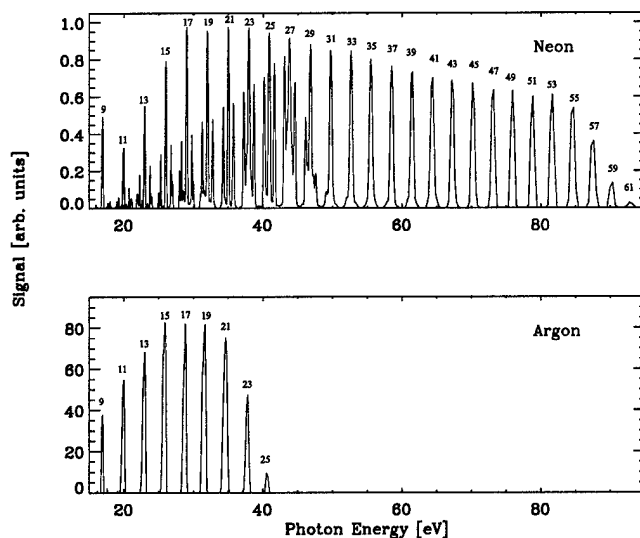


Figure 2. High harmonics generated in neon and argon. Note the lower energy cutoff in argon and the overlapping orders of the grating in the neon spectrum.

The magnetic bottle time-of-flight electron spectrometer (Fig. 1), has an additional modification to shift the kinetic energies of the electrons from high to low values by a retarding

grid system to obtain high kinetic energy resolution even for high velocity electrons. The advantages of this system are the ability to collect a large solid angle of the emitted electrons and the elimination of stray electron signals by confining the zone of collection to a very small region around the high field magnets. Figure 3 shows an example of a photoelectron spectrum of a complex molecule, Al_2Br_6 . The intrinsic resolution of our magnetic bottle is measured to be $\Delta E/E$ of 4%. A further modification to the interaction region will be made to incorporate an electron imaging system, consisting of a lensing arrangement, phosphor screen and camera, so that time-resolved ion and electron angular distributions (velocity maps) can be obtained in future experiments.

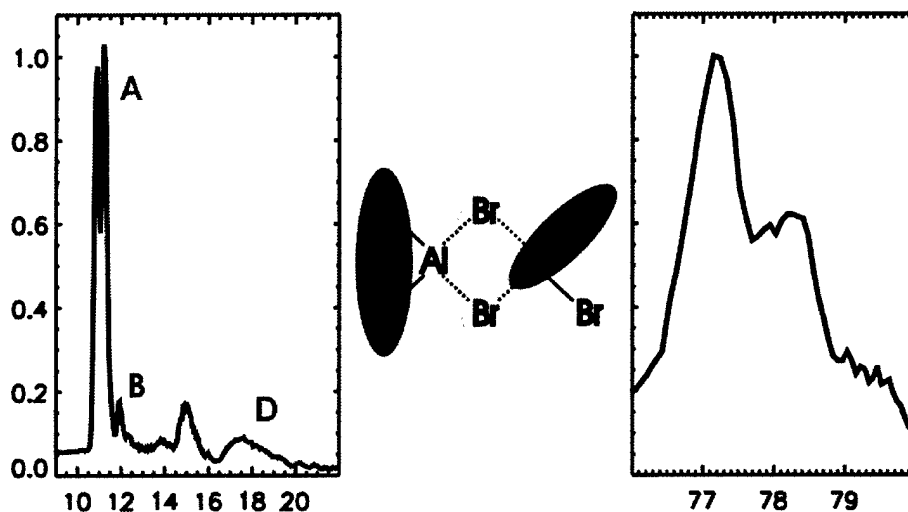


Figure 3. Photoelectron spectrum of Al_2Br_6 taken of both (left) the valence orbitals (17th harmonic of Ti:sapphire at 25 eV) and (right) the core electron energies (55th harmonic at 82 eV). A involves orbitals on the terminal Br atoms, B and D the Al-Br bonds, and C the bridge-bonded Br atoms. The energy scales are in eV.

B. Results of Ultrafast Soft X-Ray Photoelectron Probing

Results have been obtained on the photodissociation of bromine diatomic molecules with 400 nm light, by probing the vacuum ultraviolet photoelectron spectra (PES) on ultrafast timescales during the dissociation. To accomplish these experiments, first the pump pulses had to be successfully overlapped, both spatially and temporally, with the high harmonic probe pulses, and the soft x-ray pulses had to be temporally recompressed with a grating pair. A method to obtain

cross correlations with the harmonic pulses, thus, had to be established. This is accomplished by above threshold ionization (ATI), in which 800 nm or 400 nm light is incident on an atom or molecule at the same time as the ultrafast high order harmonic light. New peaks in the photoelectron spectrum are observed to higher and lower energy, as the 800 nm light adds to or subtracts from the energy of the photoelectron generated by the soft x-ray itself (Fig. 4).

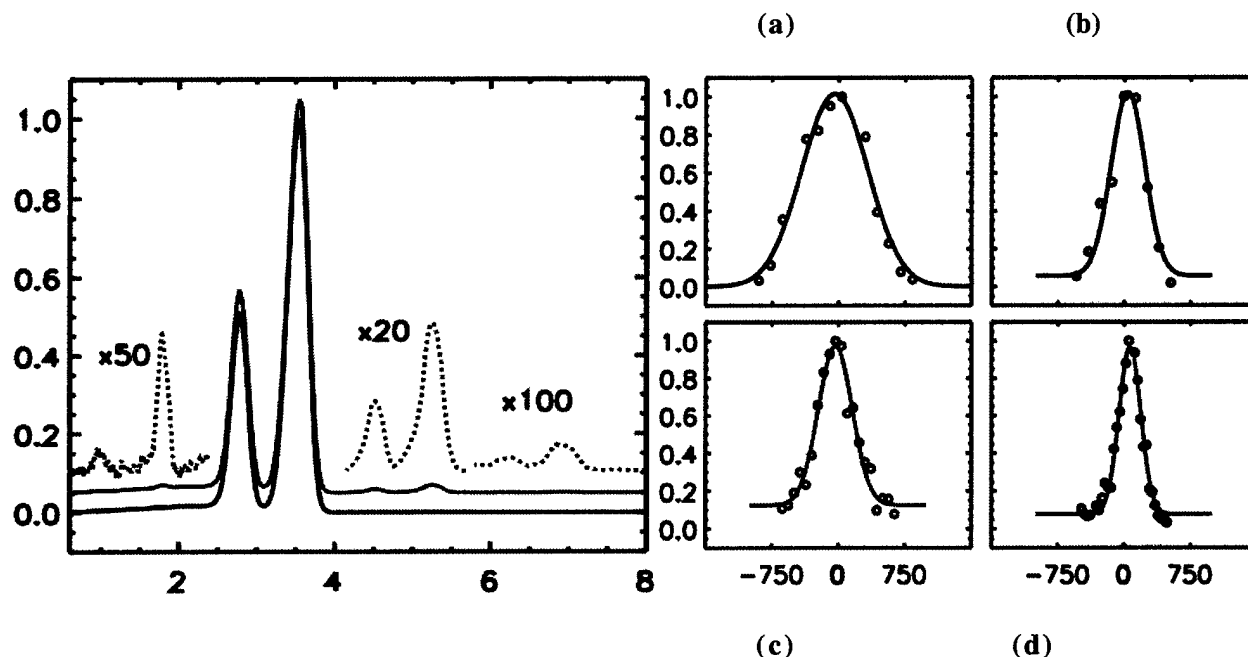


Figure 4. (Left) Above threshold ionization peaks obtained by combining 800 nm with 17th harmonic. The horizontal energy scale is in eV. (Right) Cross correlations of 400 nm pulses with the grating resolved 17th harmonic. (a) with one grating and no aperture. (b) one grating and an aperture to reduce the number of lines illuminated on the grating. (c) two gratings for recompression. (d) two gratings and an aperture. The horizontal scale is in fs. Both vertical scales are in arbitrary amplitude units.

Also shown in Fig. 4 are a series of cross correlation traces, obtained by integrating one of the ATI peaks as the time delay of one pulse is varied with respect to the other. Using one grating and with no aperture, the cross correlation is several ps. However, with two gratings arranged to recompress the wave front tilt of the light and an aperture to reduce the number of lines illuminated on the grating, pulses as short as 180 fs have been observed for the 19th harmonic. The recompression can be better-optimized at shorter wavelengths, and with better-matched grating systems, even shorter pulses from single harmonics are expected.

The first time-resolved photoelectron experiments were performed on bromine diatomic

molecules with the 17th harmonic at 25 eV as the probe (time-resolved PES). Bromine is excited with 400 nm light to the dissociative $C^1\Pi_u$ state. Figure 5 shows a sample of the time-resolved photoelectron spectra obtained during and after the dissociation event. Several significant features are notable: The two large peaks labelled $Br_2^+(X)$ and $Br_2^+(A)$ are due to the parent bromine molecules, which ionize to yield the X state and the A state of the ions. The B state of the ion is also formed, but it is not shown in these spectra. The peaks labelled 3P_2 and $^3P_{1,0}$ are due to Br atoms that are formed by the dissociation. The peaks labelled $cc(X)$ and $cc(A)$, which stands for cross correlation, can be due to above threshold ionization (ATI) peaks that occur due to the simultaneous operation of 400 nm and the 17th harmonic. However, these peaks can also arise from immediate ionization of the dissociative state, before the wave packet moves on the dissociative potential. A small feature at 8.5 eV is investigated in more detail and is assigned to the wave packet on the dissociative state, after initial excitation, but before complete dissociation.

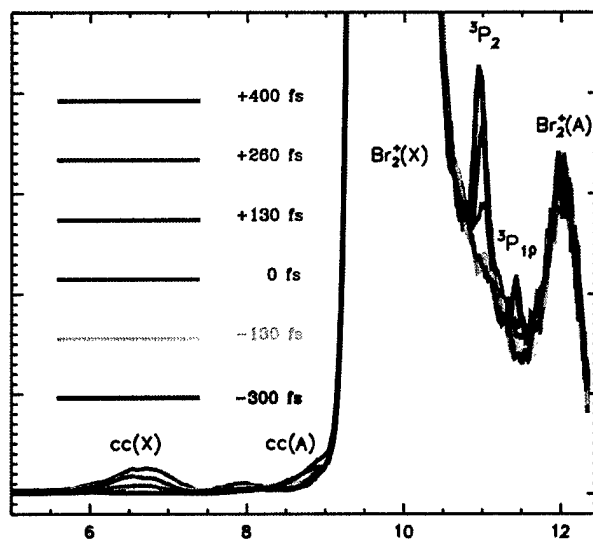


Figure 5. Time-resolved photoelectron spectra of dissociating Br_2 molecules.

As can be seen, the time-resolved soft x-ray experiments require careful analysis of small changes in signals that sit on top of large signals from undissociated background molecules. By fitting the risetime of the Br atom signals with a step function rise, the atom formation occurs in about 40 ± 10 fs. This agrees with the timescale for the Br atoms to move from the equilibrium bond distance of 2.2 Å to about 3 Å. At this distance the atoms are in the flat part of the dissociative potential and will no longer interact with each other and shift the atomic spectrum.

However, the kinds of energy shifts from the molecular to the atomic features that were expected are not observed or they are obscured by the steeply sloped, strong background spectral features of the parent molecules. Finally, ATI-like features also occur in molecules, as well as atoms.

Figure 6 shows the several processes that are observed and their locations on the potential curves in more detail: (1) represents the direct ionization of the parent molecule. (2a) is the immediate ionization of the wave packet when it is first placed on the dissociative state. (2b) is the above threshold ionization process where a 400 nm photon adds to the 17th harmonic. (3) probes the wave packet after it is formed and has had a chance to move out on the dissociative curve, but before isolated atoms occur. (4) probes the spectra of the isolated atoms.

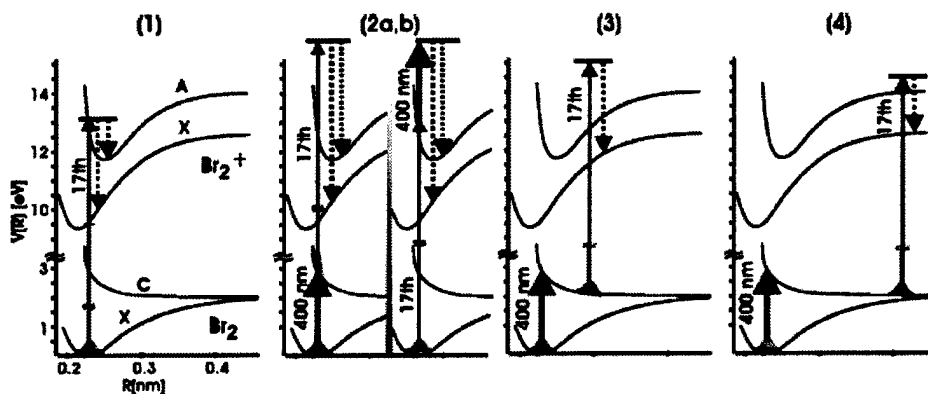


Figure 6. Schematic of the types of photoelectron spectral processes observed in the ultrafast dissociation of bromine.

Fig. 7 shows one example of data taken to study the transient wave packet on the dissociative state, depicted in panel (3) of Fig. 6. Through a large number of studies with several probe wavelengths, convincing evidence is obtained for this feature at 8.5 eV, a photoelectron energy that does not agree with any above threshold ionization or stable state processes. This feature is assigned to the wave packet on the dissociative state after it has moved to greater internuclear separation. However, this feature appears to come and go abruptly, and counter to expectation it does not shift smoothly from the energy of the ATI peak to the energy of the atoms. These results could be due to the low signal-to-noise of many features in the experiment, or the obscuring by photoelectrons from parent background features. It could also indicate some aspect of the chemical dynamics that is not yet understood.

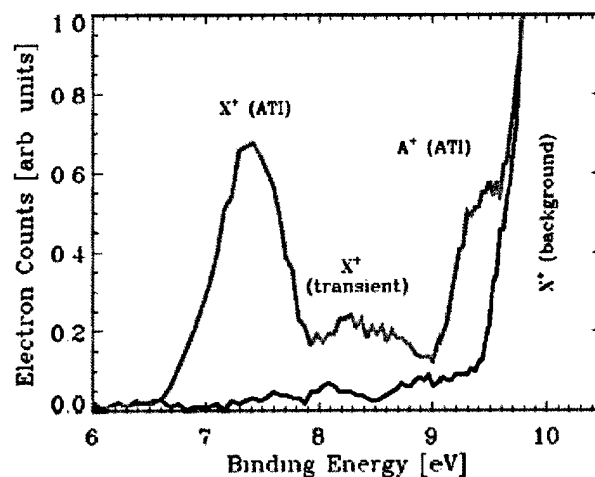


Figure 7. Photoelectron spectrum of transient wave packet in dissociating Br_2 .

An important new aspect of the information obtained in these ultrafast photoelectron experiments is the relative cross sections for the bromine molecules versus bromine atoms and the relative cross sections for the ATI features compared to the wave packet on the dissociative state. To study these aspects further, experiments were performed with a wide range of probe wavelengths, from the 13th, 15th, 17th, 19th and 21st harmonics. Figure 8 shows an example of the Br atom photoionization amplitudes with each of these harmonics, from which the relative cross sections can be obtained. In all cases, given that only a small fraction of the bromine molecules are excited by the 400 nm laser, estimates show that the Br atoms appear to be ionized more efficiently than the parent molecules, by a factor of 20-60. However, previous research suggested that the cross section for ionization of Br atoms by He(I) vacuum ultraviolet light is not that different from bromine molecules. Further work is in progress to understand this effect and to determine if multiple photon processes with the very short pulses, either in the pump or the probe step, are responsible for this difference. Comparison of the photoionization efficiencies of the ATI features with the transient wave packet feature in Fig. 7 suggests that the ATI process is an order of magnitude more efficient than direct ionization of the wave packet on the dissociative state. This new information offers many new challenges for theoretical interpretation of these two-photon events in molecules.

Finally, a preliminary experiment was performed to excite bromine molecules to a metastable excited state, the $\text{B}^3\Pi_{0_u^+}$ state and acquire the PES spectrum of this electronic state.

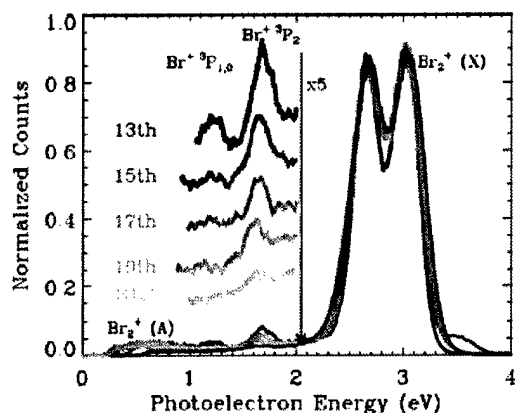


Figure 8. Time-resolved photoelectron spectra of dissociating bromine with several harmonic wavelengths as the probe.

This state lives for a number of nanoseconds, during which time a photoelectron spectrum can be obtained (Fig. 9). The excitation was accomplished with a small portion of a Nd:YLF pump laser at 527 nm. The results show a great deal of vibrational structure, because the photoelectron spectra is acquired through a high vibrational state ($v=26$) of the B state, which has a highly extended wave function and reaches different Franck Condon overlap regions with the ion states.

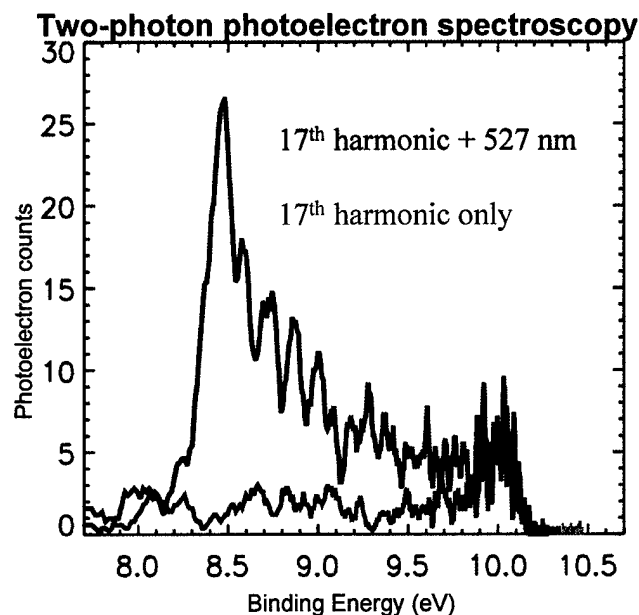


Figure 9. Photoelectron spectra of the B electronic state of bromine in $v=26$.

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Graduate Students

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Interactions/Transitions

Discussions with Roger Falcone, Thomas Baer, Nora Berrah, and Cheuk Ng concerning the production of soft x-rays by laboratory lasers and their relationship to work on pulse slicing at the Advanced Light Source geared towards developing an ultrafast x-ray source. The discussions involved issues of probing the photoelectron spectra of electronically excited states and time-resolved processes.

New discoveries, inventions, or patent disclosures

None

Honors/Awards

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Member - National Academy of Sciences

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Fellow - Optical Society of America

Fellow - American Association for the Advancement of Science

Fellow - American Academy of Arts and Sciences

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